Phosphines Functionalized with Crown Ether Groups:
Synthesis and Study of Systems Incorporating 1,3-Xylyl-18-Crown-5 Units

An Honors Thesis (HONRS 499) on Chemistry Research

by

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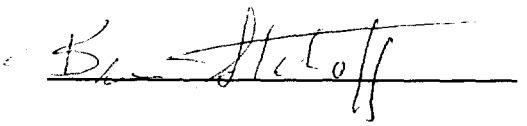

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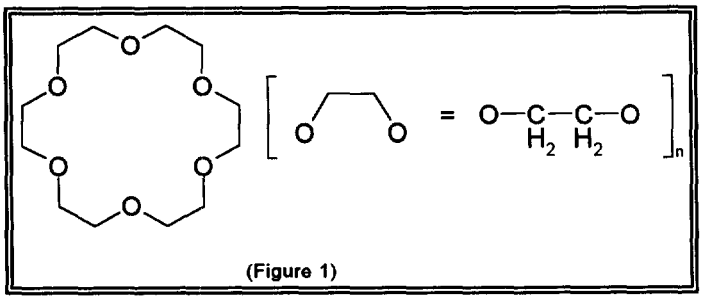
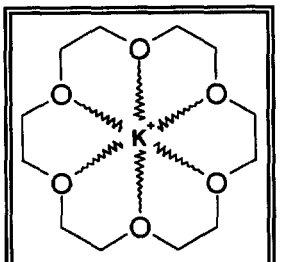
Introduction:

Although the existence of linear compounds containing ether linkages (C-O-C) has been apparent for centuries, it was not until the late 1930's that the first large ring (macrocyclic) polyethers were reported by Lüttringhaus[1]. Macrocylic polyether molecules, otherwise known as crown ether molecules, are named according to the format x-crown-y, where x is the total number of atoms in the ring and y is the number of O atoms. For example, Figure 1 is an illustration of the crown ether 18-crown-6.



(Figure 1)

In his research of these molecules and other ring structures, Lüttringhaus was able to synthesize a 20-membered crown ether compound containing six ether linkages. More recently, crown ethers were reported by Pedersen in 1967 to act as Lewis bases with a remarkable ability to form stable complexes with the salts of the alkali and alkaline earth metals found on the periodic table of elements, particularly sodium and potassium as displayed in Figure 2[2]. Although these macrocyclic polyether molecules normally have limited solubility in polar solvents such as water or methanol, Pedersen was able to show that the stable complex, formed as the crown ether molecule donates electrons to the salts of alkali and alkaline earth metals, as shown in Figure 2, helps to increase the molecular solubility. Therefore, crown ethers have special importance in being able to function in both aqueous and nonaqueous solvents. After this discovery, Pedersen continued to work in this area of chemistry producing more than 60 different crown ether molecules of various sizes and of various abilities in complexing the cationic or positively charged elements[3]. Of these newly synthesized crown ether molecules, those that contained between five and ten oxygen atoms, each



(Figure 2)

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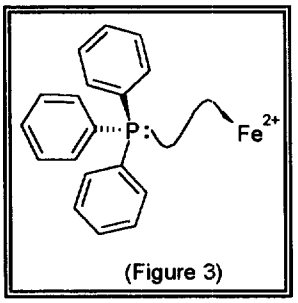
[1]A. Lüttringhaus, *Ann. Chem.*, **528**, 181 (1937).

[2]C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 2495 (1967).

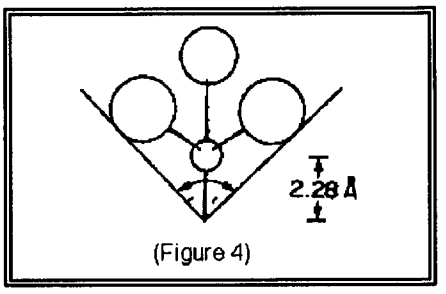
[3]C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).

separated by a bridge of two -CH_2- groups, were discovered to form the best complexes with the metal salts. Since 1967, many different crown ether molecules and their analogues have been synthesized and studied by chemists around the world, and these molecules have been found to possess distinctive characteristics in their ability to form stable complexes with a wide range of cationic species.

Additionally, a second type of Lewis base is the tertiary phosphine molecule, PR_3. These molecules are characteristically able to stabilize a wide variety of metal complexes of the form $(R_3P)_nM$-L, where L is a ligand like Cl^-, by donating the lone pair of electrons found on the phosphorus to a metal atom as shown in Figure 3. Also, they are unique in that by varying the R groups, the electronic and steric properties of the molecule can be altered in a systematic and predictable manner. The donor abilities or electronic properties of the phosphine groups depend largely on the R groups that are in the molecule. For example, a more electronegative or electron seeking R group will cause the tertiary phosphine molecule to be less basic. In contrast, a less electronegative side group will make the phosphine more basic and more likely to donate its lone pair to a metal. These differences regarding donor abilities of the phosphine can be experimentally determined by examining the infrared spectra of $R_3PNi(CO)_3$ complexes. Furthermore, the steric properties of the molecule are controlled by the type of R groups bonded to the phosphorus. In the 1970's, Tolman explained these steric properties in terms of cone angles that are based on models or X-ray structural data[4]. The simplest case of a cone angle is a symmetrical PR_3 ligand (Figure 4). In this model, the R groups are represented by the larger circles, the phosphorus by the smaller circle, and the metal complexed with the phosphine molecule is represented by the bottom of the angle. The bond distance between the phosphine molecule and the metal was established to be 2.28 Å by Tolman although this



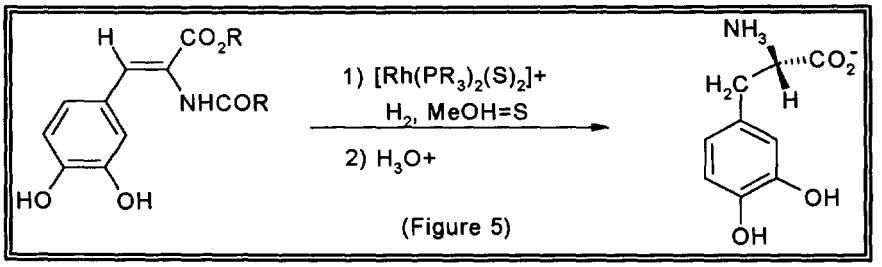
(Figure 3)



(Figure 4)

[4]C. A. Tolman, *Chem. Rev.*, **77**, 313, (1977).

distance will affect the overall magnitude of the cone angle. Phosphine ligands of the type discussed here have been used in many aspects of chemistry. An important commercial application of this use is in the organic synthesis of *L*-Dopa, which is used to treat Parkinson's disease. This compound is produced through the Monsanto process illustrated in Figure 5 that was developed by Knowles in 1983[5]. Moreover, combining the phosphine group with a crown ether molecule creates the potential for several unique chemical behaviors. The crown ether portion can bind cations such as sodium (Na^+) and potassium (K^+), and it can enhance the metal binding capabilities of the phosphorus centers[6]. Also, the crown ether and the P-donor molecules can help to impart water solubility to metal compounds in organic solvents through their phase-transfer characteristics. In addition, the organization of anions involved in reactions catalyzed by phosphine complexes could be assisted by cations like sodium and potassium complexed in tethered crown ethers. Finally, organized and localized ether solvent environments are provided by the structure of the crown ethers. These environments might help to catalyze reactions in which hard donor sites serve as hemilabile ligands or in systems where solvent organization is needed in close vicinity of the catalytic center.



(Figure 5)

Brief Description of Specific Studies and Contributions:

The focus of my work was the phosphine crown ether number 9, described on pages 7 and 8 (published manuscript). In addition to the laboratory work, I wrote part of EXPERIMENTAL section of the manuscript, and I proofread both the manuscript and the galley proofs before they were sent to the publisher of the *Organometallics* journal.

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[5]W. S. Knowles, *Accounts of Chemical Research*, **16**, 106, (1983).

[6]L. A. Barg, R. W. Byrn, M. D. Carr, D. H. Nolan, B. N. Storhoff and J. C. Huffman, *Organometallics*, **17**, 1340, (1998).

Table 1. Fractional Coordinates and Isotropic Thermal Parameters for Dipenylphosphino-1,3-xylyl-18-crown-5, Oxide

Atom	x	y	z	Biso
C(I)	2910(3)	4153(5)	-2899(6)	26
C(2)	3203(3),,	3270(5)	-2125(7)	34
O(3)	3152(2)	3265(3)	-639(4)	28
C(4)	3464(3)	2498(5)	267(7)	35
C(5)	3375(3)	2538(4)	1780(7)	36
O(6)	3706(2)	3301(3)	2652(4)	29
C(7)	3631(3)	3373(5)	4109(7)	32
C(8)	3994(2)	4188(5)	4967(6)	28
O(9)	3676(2)	5000*	4220(6)	26
C(10)	3178(4)	5000*	-2269(9)	25
C(11)	2354(3)	4169(5)	-4220(6)	31
C(12)	2083(4)	5000*	-4872(10)	37
P(13)	1354(I)	5297(2)	-6502(3)	22
O(14)	1058(5)	6216(8)	-6435(12)	28
C(15)	1541(4)	5000*	-8217(9)	33
C(16)	1052(4)	4778(10)	-9639(12)	27
C(17)	1165(5)	4878(80)	-10999(11)	28
C(18)	1770(4)	5000*	-10944(9)	25
C(19)	2267(4)	5000*	-9547(9)	26
C(20)	2149(3)	5000*	-8193(8)	20
C(21)	853(6)	4344(10)	-6443(14)	20
C(22)	608(5)	4339(9)	-5270(12)	30
C(23)	209(5)	3645(11)	-5139(15)	40
C(24)	36(5)	2945(10)	-6220(16)	36
C(25)	276(11)	2953(13)	-7424(33)	38
C(26)	681(6)	3629(9)	-7510(15)	24
C(0I)	4193(4)	5000*	1576(10)	34
C(02)	4654(7)	4086(20)	1791(17)	92
C(03)	5046(15)	3957(12)	592(33)	95
C(04)	203(30)	7325(53)	-8154(114)	205
C(05)	56(14)	7039(21)	-8559(44)	52
H(I)	295*	276*	-278*	47
H(2)	362*	321*	-213*	47
H(3)	330*	193*	-28*	47
H(4)	391*	252*	43*	47
H(5)	292*	261*	159*	50
H(6)	350*	197*	235*	50
H(7)	318*	345*	392*	45
H(8)	377*	281*	468*	45
H(9)	401*	418*	602*	43
H(10)	441*	418*	498*	43
H(11)	362*	500*	-92*	43

Notes:

1) Fractional coordinates are X 10*4 for non-hydrogen atoms and X 10*3 for hydrogen atoms.

2) Biso values are X 10.

3) Isotropic values for those atoms refined anisotropically are calculated using the formula given by W. C. Hamilton, Acta Cryst. 1959, 12, 609.

4) Parameters marked by an asterisk were not varied.

Table 1. Fractional Coordinates and Isotropic Thermal Parameters for Dipenylphosphino-1,3-xylyl-18-crown-5, Oxide

H(12)	216*	358*	538*	44
H(13)	64*	461*	-970*	40
H(14)	82*	475*	-1194*	18
H(15)	184*	489*	-1190*	38
H(16)	269*	500*	-955*	39
H(17)	251*	500*	-719*	36
H(18)	73*	484*	-448*	50
H(19)	2*	362*	-438*	64
H(20)	-24*	243*	-618*	52
H(21)	14*	248*	-828*	37
H(22)	85*	359*	-832*	38

Notes:

1) Fractional coordinates are X 10*4 for non-hydrogen atoms and X 10*3 for hydrogen atoms.

2) Biso values are X 10.

3) Isotropic values for those atoms refined anisotropically are calculated using the formula given by W. C. Hamilton, Acta Cryst. 1959, 12, 609.

4) Parameters marked by an asterisk were not varied.

Table 2. Anistropic Thermal Parameters for Diphenylphosphino-1,3-xylyl-18-crown-5, Oxide

Atom	b11	b22	b33	b12	b13	b23
C(1)	16(1)	37(4)	80(8)	0(2)	22(3)	-4(5)
C(2)	22(2)	43(4)	119(10)	-1(2)	34(4)	-9(6)
O(3)	18(1)	33(2)	93(7)	3(1)	18(2)	2(3)
C(4)	22(2)	36(4)	109(10)	6(2)	14(4)	1(6)
C(5)	25(2)	27(4)	112(10)	-3(2)	10(4)	5(6)
O(6)	18(1)	36(3)	86(6)	0(1)	16(2)	2(3)
C(7)	22(2)	39(4)	90(10)	4(2)	21(3)	21(5)
C(8)	15(1)	44(4)	84(9)	2(2)	16(3)	10(6)
O(9)	12(1)	34(4)	87(9)	0*	8(3)	0*
C(10)	18(2)	38(6)	65(12)	0*	27(4)	0*
C(11)	16(2)	60(4)	75(9)	-10(2)	24(3)	-31(6)
C(12)	17(2)	81(8)	64(14)	0*	20(5)	0*
P(13)	14(1)	30(2)	60(4)	-2(1)	14(1)	-3(2)
O(14)	20(3)	33(6)	77(15)	7(4)	20(6)	-10(9)
C(15)	14(2)	69(7)	56(13)	0*	13(5)	0*
C(16)	14(2)	39(16)	83(15)	3(4)	18(5)	2(10)
C(17)	17(2)	41(50)	63(13)	-9(10)	11(5)	6(17)
C(18)	21(2)	31(5)	63(13)	0*	27(5)	0*
C(19)	16(2)	40(6)	87(14)	0*	26(5)	0*
C(20)	13(2)	22(4)	55(12)	0*	6(4)	0*
C(21)	8(3)	36(9)	45(18)	-7(4)	5(6)	4(11)
C(22)	15(3)	51(8)	76(17)	-3(4)	15(6)	7(10)
C(23)	15(4)	81(11)	120(21)	-3(5)	31(7)	7(14)
C(24)	12(3)	54(9)	138(22)	-6(4)	15(7)	16(13)
C(25)	18(5)	43(11)	151(43)	-1(5)	18(13)	-3(14)
C(26)	10(3)	43(8)	60(18)	-4(4)	10(6)	6(11)
C(01)	19(2)	52(6)	94(14)	0*	20(5)	0*
C(02)	21(4)	230(26)	125(25)	-21(9)	4(8)	-24(22)
C(03)	58(7)	72(11)	617(103)	9(10)	175(29)	16(25)
C(04)	41(14)	405(88)	609(162)	10(30)	26(39)	-1(108)
C(05)	16(5)	93(17)	156(45)	12(7)	11(14)	15(20)

Form of the bij anisotropic thermal parameter:
exp[-(h**2b11+...+2hkb12+...)]
All values are X 10**4.

Table 3. Anisotropic Thermal Parameters for Diphenylphosphino-1,3-xylyl-18-crown-5, Oxide

Atom	U11	U22	U33	U12	U13	U23
C(l)	35(3)	39(4)	30(3)	0(3)	21(3)	-2(3)
C(2)	50(4)	45(5)	45(4)	-1(4)	32(3)	-6(4)
0(3)	40(2)	35(3)	35(2)	5(2)	16(2)	1(2)
C(4)	50(4)	38(4)	41(4)	10(3)	12(3)	1(4)
C(5)	57(4)	29(4)	42(4)	-4(4)	10(3)	3(4)
0(6)	42(2)	38(3)	33(2)	-1(2)	15(2)	1(2)
C(7)	49(4)	41(4)	34(4)	7(3)	19(3)	13(3)
C(8)	33(3)	46(4)	32(3)	3(3)	15(3)	7(3)
O(9)	26(3)	35(4)	33(3)	0*	7(3)	0*
C(10)	40(5)	40(6)	25(5)	0*	25(4)	0*
C(11)	37(4)	63(5)	28(3)	-15(4)	23(3)	-20(4)
C(12)	38(5)	85(9)	24(5)	0*	19(4)	0*
P(13)	31(2)	31(3)	23(2)	-4(l)	13(l)	-2(l)
O(14)	45(6)	35(6)	29(6)	10(5)	18(5)	-6(6)
C(15)	32(5)	73(7)	21(5)	0*	12(4)	0*
C(16)	33(6)	41(17)	31(6)	5(6)	16(5)	2(6)
C(17)	39(5)	43(53)	24(5)	-13(16)	11(4)	4(11)
C(18)	47(5)	32(5)	24(5)	0*	25(4)	0*
C(19)	35(5)	42(6)	33(5)	0*	24(4)	0*
C(20)	29(5)	23(5)	21(5)	0*	5(4)	0*
C(21)	19(7)	38(9)	17(7)	-10(7)	5(6)	3(7)
C(22)	33(6)	53(9)	29(6)	-5(6)	14(6)	5(6)
C(23)	35(8)	85(11)	46(8)	-4(7)	29(7)	4(9)
C(24)	28(7)	57(10)	52(8)	-9(7)	14(7)	10(8)
C(25)	40(10)	46(11)	57(16)	-2(8)	16(12)	-2(9)
C(26)	23(6)	46(9)	23(7)	-6(7)	10(6)	4(7)
C(0l)	43(6)	54(7)	36(5)	0*	19(5)	0*
C(02)	47(9)	242(27)	47(10)	-32(13)	3(8)	-15(14)
C(03)	132(15)	76(12)	234(39)	14(15)	162(27)	10(16)
C(04)	93(33)	427(93)	231(61)	15(46)	24(36)	-1(68)
C(05)	36(12)	98(18)	59(17)	19(11)	10(13)	9(13)

Form of the Uij anisotropic thermal parameter:
exp[-2(pi)**2[h**2(a*)**2U11+...+hka*b*U12+...]]
All values are X 10**3.

Table 4. Bond Distances

A	B	Distance
O(3)	C(2)	1.423(6)
O(3)	C(4)	1.415(3)
O(6)	C(5)	1.412(3)
O(6)	C(7)	1.425(6)
O(9)	C(8)	1.418(3)
O(14)	C(21)	0.930(9)
O(14)	C(21)	0.930(9)
O(14)	C(22)	1.907(14)
O(14)	C(26)	1.077(10)
O(14)	P(13)	1.496(5)
C(02)	C(03)	1.66(3)
C(03)	C(03)	1.040(24)
C(04)	C(05)	0.58(4)
P(13)	P(13)	0.8574(4)
C(1)	C(2)	1.495(3)
C(1)	C(10)	1.396(3)
C(1)	C(11)	1.406(6)
C(4)	C(5)	1.488(8)
C(7)	C(8)	1.490(3)
C(11)	C(12)	1.383(4)
C(12)	P(13)	1.843(6)
C(15)	C(16)	1.420(8)
C(15)	C(20)	1.369(11)
C(15)	P(13)	1.837(5)
(16)	C(16)	0.6404(3)
C(16)	C(17)	1.38(7)
C(16)	C(17)	1.46(7)
C(17)	C(17)	0.3506(1)
C(17)	C(18)	1.363(26)
C(18)	C(19)	1.377(5)
C(19)	C(20)	1.374(6)
C(21)	C(21)	1.8933(8)
C(21)	C(22)	1.386(18)
C(21)	C(26)	1.384(8)
C(21)	P(13)	1.266(13)
C(21)	P(13)	1.796(9)
C(22)	C(22)	1.9070(8)
C(22)	C(23)	1.382(12)
C(23)	C(23)	1.067(26)
C(23)	C(24)	1.377(8)
C(23)	C(24)	1.849(14)
C(23)	C(24)	1.849(14)
C(24)	C(25)	1.405(25)
C(24)	C(04)	2.00(6)
C(25)	C(26)	1.361(21)
C(25)	C(04)	0.75(4)

A	B	Distance
C(25)	C(05)	.989(21)
C(26)	C(04)	1.72(3)
C(26)	C(04)	1.72(3)
C(26)	C(05)	1.700(23)
C(26)	C(05)	1.700(23)
C(26)	P(13)	2.137(8)
C(01)	C(02)	1.647(10)
C(01)	C(02)	1.647(10)
C(2)	H(1)	0.99
C(2)	H(2)	0.94
C(4)	H(3)	0.96
C(4)	H(4)	0.97
C(5)	H(5)	0.97
C(5)	H(6)	0.96
C(7)	H(7)	0.96
C(7)	H(8)	0.95
C(8)	H(9)	0.96
C(8)	H(10)	0.94
C(10)	H(11)	1.28
C(11)	H(12)	0.96
C(16)	H(13)	0.95
C(16)	H(13)	1.27
C(17)	H(14)	0.96
C(17)	H(14)	1.08
C(18)	H(15)	0.96
C(19)	H(16)	0.96
C(20)	H(17)	0.98
C(22)	H(18)	0.99
C(22)	H(18)	1.37
C(23)	H(19)	0.55
C(23)	H(19)	0.94
C(24)	H(19)	1.15
C(24)	H(19)	1.15
C(24)	H(20)	0.98
C(25)	H(21)	1.01
C(26)	H(22)	0.95
C(04)	H(21)	0.32
C(04)	H(21)	0.32
C(05)	H(21)	0.74
H(14)	H(14)	0.73
H(15)	H(15)	0.32
H(18)	H(18)	0.47

Table 5. Bond Angles

A	B	C	Angle
C(2)	O(3)	C(4)	112.4(3)
C(5)	O(6)	C(7)	112.3(3)
C(8)	O(9)	C(8)	111.4(3)
C(21)	O(14)	C(22)	43.4(10)
C(21)	O(14)	C(26)	86.9(9)
C(21)	O(14)	P(13)	57.4(8)
C(22)	O(14)	C(26)	101.8(9)
C(22)	O(14)	P(13)	89.4(3)
C(26)	O(14)	P(13)	111.3(4)
C(2)	C(1)	C(10)	119.6(3)
C(2)	C(1)	C(11)	122.42(21)
C(10)	C(1)	C(11)	117.90(22)
O(3)	C(2)	C(I)	107.0(3)
O(3)	C(4)	C(5)	108.7(3)
O(6)	C(5)	C(4)	110.2(4)
O(6)	C(7)	C(8)	109.4(4)
O(9)	C(8)	C(7)	107.8(3)
C(1)	C(10)	C(1)	122.3(4)
C(1)	C(11)	C(12)	120.85(26)
C(11)	C(12)	C(11)	120.2(5)
C(11)	C(12)	P(13)	133.3(3)
C(11)	C(12)	P(13)	106.41(24)
C(11)	C(12)	P(13)	133.3(3)
P(13)	C(12)	P(13)	26.90(9)
C(16)	C(15)	C(16)	26.06(16)
C(16)	C(15)	C(20)	117.4(5)
C(16)	C(15)	P(13)	120.6(7)
C(16)	C(15)	P(13)	113.9(6)
C(16)	C(15)	P(13)	120.6(7)
C(20)	C(15)	P(13)	121.97(23)
P(13)	C(15)	P(13)	26.99(8)
C(15)	C(16)	C(16)	76.97(8)
C(15)	C(16)	C(17)	119.0(10)
C(15)	C(16)	C(17)	113.8(11)
C(16)	C(16)	C(17)	84.0(3)
C(16)	C(16)	C(17)	70.2(10)
C(17)	C(16)	C(17)	13.8(7)
C(16)	C(17)	C(16)	25.9(13)
C(16)	C(17)	C(17)	96.0(3)
C(16)	C(17)	C(17)	70.2(10)
C(16)	C(17)	C(18)	120.(4)
C(16)	C(17)	C(18)	114.(3)
C(17)	C(17)	C(18)	82.61(14)
C(17)	C(18)	C(17)	14.8(3)
C(17)	C(18)	C(19)	120.(3)
C(18)	C(19)	C(20)	119.8(7)
C(15)	C(20)	C(19)	120.7(4)
O(14)	C(21)	C(21)	150.2(10)
O(14)	C(21)	C(22)	109.2(10)
O(14)	C(21)	C(26)	51.0(7)
O(14)	C(21)	P(13)	110.2(13)

O(14)	C(21)	P(13)	84.4(13)
C(21)	C(21)	C(22)	90.283(4)
C(21)	C(21)	C(26)	138.1(4)
C(21)	C(21)	P(13)	40.0(4)
C(21)	C(21)	P(13)	65.85(27)
C(22)	C(21)	C(26)	117.9(9)
C(22)	C(21)	P(13)	130.8(6)
C(22)	C(21)	P(13)	117.6(4)
C(26)	C(21)	P(13)	124.5(11)
C(26)	C(21)	P(13)	107.4(12)
P(13)	C(21)	P(13)	25.82(9)
O(14)	C(22)	C(21)	27.43(25)
O(14)	C(22)	C(22)	114.82(20)
O(14)	C(22)	C(23)	104.2(5)
C(21)	C(22)	C(22)	89.717(4)
C(21)	C(22)	C(23)	122.0(6)
C(22)	C(22)	C(23)	136.4(5)
C(22)	C(23)	C(23)	133.3(5)
C(22)	C(23)	C(24)	119.4(11)
C(22)	C(23)	C(24)	145.2(7)
C(23)	C(23)	C(24)	47.6(7)
C(23)	C(23)	C(24)	97.5(10)
C(24)	C(23)	C(24)	91.1(7)
C(23)	C(24)	C(23)	34.9(9)
C(23)	C(24)	C(25)	146.3(3)
C(23)	C(24)	C(25)	118.8(9)
C(23)	C(24)	C(04)	156.5(6)
C(23)	C(24)	C(04)	134.4(13)
C(25)	C(24)	C(04)	15.9(16)
C(24)	C(25)	C(26)	121.0(7)
C(24)	C(25)	C(04)	133.(6)
C(24)	C(25)	C(05)	130.8(27)
C(26)	C(25)	C(04)	105.(6)
C(26)	C(25)	C(05)	91.3(16)
C(04)	C(25)	C(05)	35.5(25)
O(14)	C(26)	C(21)	42.1(6)
O(14)	C(26)	C(25)	114.9(8)
O(14)	C(26)	C(04)	132.6(13)
O(14)	C(26)	C(05)	150.1(8)
O(14)	C(26)	P(13)	40.7(3)
C(21)	C(26)	C(25)	120.9(12)
C(21)	C(26)	C(04)	145.5(24)
C(21)	C(26)	C(05)	142.5(15)
C(21)	C(26)	P(13)	34.4(7)
C(25)	C(26)	C(04)	25.0(22)
C(25)	C(26)	C(05)	35.6(8)
C(25)	C(26)	P(13)	152.0(8)
C(04)	C(26)	C(05)	19.4(15)
C(04)	C(26)	P(13)	172.9(13)
C(05)	C(26)	P(13)	167.8(6)
C(02)	C(Ol)	C(02)	106.3(9)
C(01)	C(02)	C(03)	118.4(9)
C(02)	C(03)	C(03)	139.(4)
C(24)	C(04)	C(25)	31.(5)
C(24)	C(04)	C(26)	80.3(16)
C(24)	C(04)	C(05)	101.(8)
C(25)	C(04)	C(26)	50.(4)
C(25)	C(04)	C(05)	95.(5)
C(26)	C(04)	C(05)	78.(4)

C(25)	C(05)	C(26)	53.2(14)
C(25)	C(05)	C(04)	49.(5)
C(26)	C(05)	C(04)	82.(6)
O(14)	P(13)	C(12)	117.0(3)
O(14)	P(13)	C(15)	119.3(3)
O(14)	P(13)	C(21)	112.3(5)
O(14)	P(13)	C(21)	38.2(5)
O(14)	P(13)	C(26)	28.0(3)
O(14)	P(13)	P(13)	152.3(4)
C(12)	P(13)	C(15)	103.8(3)
C(12)	P(13)	C(21)	100.7(3)
C(12)	P(13)	C(21)	127.7(5)
C(12)	P(13)	C(26)	144.51(19)
C(12)	P(13)	P(13)	76.55(5)
C(15)	P(13)	C(21)	101.1(4)
C(15)	P(13)	C(21)	128.5(4)
C(15)	P(13)	C(26)	98.1(3)
C(15)	P(13)	P(13)	76.50(4)
C(21)	P(13)	C(21)	74.1(6)
C(21)	P(13)	C(26)	102.1(4)
C(21)	P(13)	C(26)	38.2(5)
C(21)	P(13)	P(13)	40.0(4)
C(21)	P(13)	P(13)	114.15(27)
C(26)	P(13)	P(13)	136.43(22)
O(3)	C(2)	H(1)	111.0
O(3)	C(2)	H(2)	115.7
C(1)	C(2)	H(1)	106.4
C(1)	C(2)	H(2)	110.0
H(1)	C(2)	H(2)	106.4
O(3)	C(4)	H(3)	109.8
O(3)	C(4)	H(4)	109.9
C(5)	C(4)	H(3)	112.3
C(5)	C(4)	H(4)	109.8
H(3)	C(4)	H(4)	106.4
O(6)	C(5)	H(5)	109.2
O(6)	C(5)	H(6)	111.1
C(4)	C(5)	H(5)	108.8
C(4)	C(5)	H(6)	111.3
H(5)	C(5)	H(6)	106.1
O(6)	C(7)	H(7)	107.9
O(6)	C(7)	H(8)	109.7
C(8)	C(7)	H(7)	110.3
C(8)	C(7)	H(8)	111.5
H(7)	C(7)	H(8)	107.9
O(9)	C(8)	H(9)	109.5
O(9)	C(8)	H(I0)	110.5
C(7)	C(8)	H(9)	110.1
C(7)	C(8)	H(10)	110.4
H(9)	C(8)	H(I0)	108.6
C(1)	C(10)	H(11)	118.3
C(1)	c(11)	H(12)	117.1
C(12)	C(11)	H(12)	122.0
C(15)	C(16)	H(13)	122.5
C(15)	C(16)	H(13)	101.7
C(16)	C(16)	H(13)	104.7
C(16)	C(16)	H(13)	46.2
C(17)	C(16)	H(13)	118.3

C(17)	C(16)	H(13)	105.2
C(17)	C(16)	H(13)	94.7
C(17)	C(16)	H(13)	120.7
H(13)	C(16)	H(13)	58.5
C(16)	C(17)	H(14)	118.0
C(16)	C(17)	H(14)	117.0
C(16)	C(17)	H(14)	103.0
C(16)	C(17)	H(14)	120.9
C(17)	C(17)	H(14)	101.5
C(17)	C(17)	H(14)	60.1
C(18)	C(17)	H(14)	123.0
C(18)	C(17)	H(14)	113.0
H(14)	C(17)	H(14)	41.4
C(17)	C(18)	H(15)	116.0
C(17)	C(18)	H(15)	119.0
C(17)	C(18)	H(15)	116.0
C(19)	C(18)	H(15)	120.8
H(15)	C(18)	H(15)	19.4
C(18)	C(19)	H(16)	118.4
C(20)	C(19)	H(16)	121.8
C(15)	C(20)	H(17)	119.4
C(19)	C(20)	H(17)	119.9
O(14)	C(22)	H(18)	131.5
O(14)	C(22)	H(18)	128.6
C(21)	C(22)	H(18)	110.9
C(21)	C(22)	H(18)	119.7
C(22)	C(22)	H(18)	43.5
C(22)	C(22)	H(18)	29.8
C(23)	C(22)	H(18)	118.3
C(23)	C(22)	H(18)	126.2
H(18)	C(22)	H(18)	13.6
C(22)	C(23)	H(19)	116.1
C(22)	C(23)	H(19)	125.4
C(23)	C(23)	H(19)	61.9
C(23)	C(23)	H(19)	31.2
C(24)	C(23)	H(19)	54.7
C(24)	C(23)	H(19)	94.6
C(24)	C(23)	H(19)	115.1
C(24)	C(23)	H(19)	31.1
H(19)	C(23)	H(19)	92.8
C(23)	C(24)	H(19)	23.1
C(23)	C(24)	H(19)	25.0
C(23)	C(24)	H(20)	92.2
C(23)	C(24)	H(20)	123.3
C(25)	C(24)	H(19)	121.4
C(25)	C(24)	H(20)	118
C(04)	C(24)	H(19)	133.7
C(04)	C(24)	H(20)	102.3
H(19)	C(24)	H(20)	115.9
C(24)	C(25)	H(21)	121.3
C(26)	C(25)	H(21)	117.4
C(04)	C(25)	H(21)	13
C(05)	C(25)	H(21)	43.7
O(14)	C(26)	H(22)	109.5
C(21)	C(26)	H(22)	121.3

C(25)	C(26)	H(22)	117.8
C(04)	C(26)	H(22)	93.1
C(05)	C(26)	H(22)	89.9
P(13)	C(26)	H(22)	88.2
C(24)	C(04)	H(21)	107
C(25)	C(04)	H(21)	136
C(26)	C(04)	H(21)	169
C(05)	C(04)	H(21)	108
C(25)	C(05)	H(21)	69.9
C(26)	C(05)	H(21)	106.4
C(04)	C(05)	H(21)	24

Indiana Academy of Science Presentation Abstract- Chemistry (1997):

PHOSPHINES FUNCTIONALIZED WITH CROWN ETHER GROUPS: THE SYNTHESIS AND STUDY OF SYSTEMS INCORPORATING 1,3-XYLYL-18-CROWN-5 UNITS. Lisa A. Barg, Robert W. Byrn, Michael D. Carr, Daniel H. Nolan and **Bruce N. Storhoff**. Department of Chemistry, Ball State University, Muncie, IN 47306-0445, and John C. Huffman, Indiana University, Molecular Structure Center, Bloomington, IN 47405-4001.

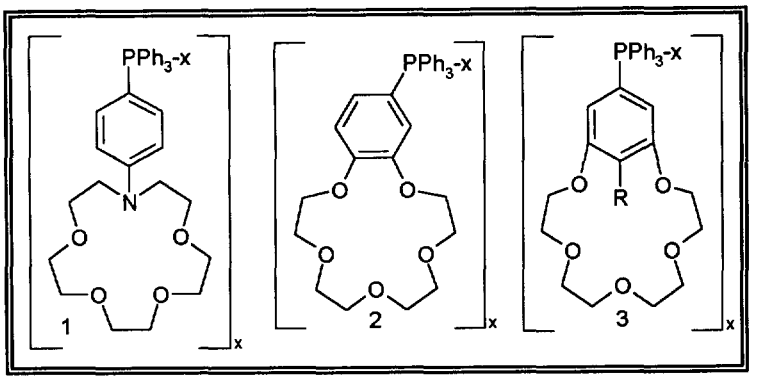
Hybrid phosphine-crown ether molecules have been synthesized from Ph_2PCl, $PhP(OMe)_2$ or $P(OPh)_3$ and the carbanions generated by lithium/bromide exchange reactions between n-butyl lithium and 5-bromo-1,3-xylyl-18-crown-5 or 5-bromo-2-methoxy-1,3-xylyl-18-crown-5. With these phosphine systems represented as $Ph_xP(crown)_{3-x}$, the x = 0 - 2 and 1 - 2 members are reported for the former and latter crown ethers, respectively. The molecular structure, from X-ray crystallographic studies, of the oxide of the phosphine with x = 2 and a H in the 2 position has been obtained, and the structural features associated with the crown ether portion of the molecule will be discussed.

PHOSPHINES FUNCTIONALIZED WITH CROWN ETHER GROUPS: THE PROPERTIES OF SYSTEMS INCORPORATING 1,3-XYLYL-18-CROWN-5 UNITS. Lisa A. Barg, Robert W. Byrn, Michael D. Carr, Daniel H. Nolan and **Bruce N. Storhoff**. Department of Chemistry, Ball State University, Muncie, IN 47306-0445.

The steric and electronic properties of five phosphines functionalized with 1,3-Xylyl-18-Crown-5 Units have been investigated by studying the spectroscopic characteristics of Ni and Pd complexes of the P(III) ligated systems. The Al μ(CO) stretching frequencies from the $Ni(CO)_3L$ (L = $Ph_xP(crown)_{3-x}$) complexes are within 0.4 cm^{-1} of 2068.9 cm^{-1}, the value for the $Ni(CO)_3PPh_3$. For both series of ligands, H or OMe in the 2 position, the μ(CO) stretching frequencies are found to decrease with increasing substitution by crown ether groups (decreasing x). The addition of Na^+ - Cs^+ (SCN^- salts) to the Ni complexes cause the Al bands to shift to higher frequencies and to broaden. The largest shifts were observed for Na^+ ions with phosphines substituted with larger numbers of crown ether groups. ^{31}P NMR spectral data for the L_2PdCl_2 complexes of these phosphines range between 22 and 25 ppm, values that are considered consistent with cone angles of ca. 145°.

American Chemical Society Abstract - *30th HLRM (Chicago)*:

THE SYNTHESIS AND STUDY OF PHOSPHINES FUNCTIONALIZED WITH BENZO, AZA OR XYLYL CROWN SYSTEMS. Lisa A. Barg, Michael D. Carr, Stephen A. Erickson, Matthew T. Mizwicki, Daniel H. Nolan, and **Bruce N. Storhoff**, Department of Chemistry, Ball State University, Muncie, IN 47306.



Phosphines functionalized with crown ethers provide a basis for obtaining complexes with, for example, phase transfer properties, tunable electron densities, and recovery sites. Recently we have been investigating the properties of three phosphines that are functionalized with either crown-5 or crown-6 groups. The entire series of 1 (crown 5) as well as the X = 1 and 2 members of 2 and 3 have been synthesized. Infrared studies of the $Ni(CO)_3L$ complexes of 1-3 indicate that the phosphorus donor abilities are 1 > 2 > 3, an outcome that can be predicted by using Hammet or Drago E and C parameters. Further, X-ray data from the oxides of 1 (X = 3) and 3 (X = 1) are consistent with the conclusion that the cone angles of these phosphines are similar to that of triphenylphosphine. Additional aspects of the X-ray data and effects of added ions on the v(CO) values as well as specific outcomes of Drago's E and C parameter calculations will also be presented.

American Chemical Society Abstract - *31st HLRM (Milwakee)*:

THE SYNTHESIS AND STUDY OF PHOSPHINES FUNCTIONALIZED WITH XYLYL CROWN ETHER GROUPS. **Bruce N. Storhoff**, Michael D. Carr, Daniel H. Nolan and Robert W. Bym, Department of Chemistry, Ball State University, Muncie, IN 47306.

1,3-Xylyl-18-Crown-5 ethers functionalized in the 2 position with OMe, OH, or F groups and in the 5 position with P(III) centers have been synthesized and studied. With these phosphine systems represented as $Ph_xP(crown)_{3-x}$, members of the x = 1 and 2 series of the systems with OMe and OH interannular substituents have been synthesized and studied whereas the x = 1 member of the F-containing group has been obtained. All were synthesized from chlorodiphenylphosphine or dimethyl phenylphosphonite and the carbanions generated by lithium/bromide exchange reactions between n-butyl lithium and the 5-bromo-1,3-xylyl-18-crown-5 starting materials. The donor properties of these phosphines have been studied by measuring the carbonyl stretching frequencies of the corresponding nickel tricarbonyl complexes. One outcome is that the OMe groups do not appear to have the expected (Hammett substituent effect) electron donating effects.